

Electronic Supplementary Information (ESI) for

Insights into the reactive and deactivation mechanisms of manganese oxides for the ozone elimination: the roles of surface oxygen species

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1. Details on the catalyst preparation

Chemicals and reagents: $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). NaOH, 30% H_2O_2 and absolute ethanol was purchased from Kermel (Tianjin, China). All chemicals were analytical grade and used without further purification.

Preparation of γ -MnOOH: The pristine γ -MnOOH nanorod was synthesized by a redox precipitation process. In a typical synthesis, 6.127g $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in deionized water. 20mL 30% H_2O_2 was poured to 50mL of 1M NaOH aqueous solution, then the NaOH- H_2O_2 solution was slowly added to the above $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ aqueous solution under vigorous stirring. Finally, the as-obtained solution was stirred at 60°C for 12 h. A brown solid was obtained by hot filtration, which was washed with deionized water and absolute ethanol for several times, finally dried in a vacuum at 60°C for 12 h.

Preparation of manganese oxides with different valances: Typically, β - MnO_2 was prepared by calcining γ -MnOOH precursors at 350°C for 4 h in air. When the temperature reached to 600°C, α - Mn_2O_3 was obtained. And Mn_3O_4 could be prepared via treating γ -MnOOH at 600°C for 2 h in Ar. A certain amount of MnO_2 was treated at 200°C for 2h under a 10 vol% H_2 /Ar gas flow, which was denoted as MnO_2 -H-200.

2. Details on the catalyst characterization

The crystalline structure was characterized by X-ray diffraction (PANalytical Empyrean-100, $\text{CuK}\alpha=1.54056 \text{ \AA}$). The morphology of the samples was observed by a JSM-7800F field emission scanning electron microscopy with an accelerating voltage

of 3 kV. And the transmission electron microscopy was done on a JEM-2000. The Raman spectra were recorded on a microscopic confocal Raman spectrometer (Bruker Optics Senterra). X-ray photoelectron spectroscopy was measured in an ESCALAB 250Xi spectrometer and the binding energy was calibrated with the signal for adventitious carbon at 284.6 eV. The specific surface areas were determined by N₂-adsorption isotherms using a NOVA2200e instrument. All samples were pretreated at 150°C for 3h under high vacuum. BET specific surface area was calculated by the BET method according to the adsorption branch in the relative pressure range from 0.05 to 0.35.

Programmed temperature reduction or desorption experiments (TPR or TPD) were carried out using Quantachrome ChemiBET 3000 adsorption instrument equipped with a TCD detector. In H₂-TPR experiment, 20 mg samples were loaded in a quartz reactor, pretreated at 200°C for 2h under He gas flow, and cooled to 25°C, following which the samples were heated to 700°C with a 10 vol% H₂/Ar gas flow at a heat rate of 10°C min⁻¹. In O₂-TPD experiment, 50mg samples were pretreated at 200°C for 2h under He gas flow, and then cooled to 25°C. Afterwards, the samples were purged with a mixture of 3 vol% O₂/He at 25°C for 2h. Desorption of O₂ was carried out from 25°C to 900°C at a heating rate of 5°C min⁻¹ purged with He. In O₃-TPD experiment after ozone adsorption, 50mg catalysts were pretreated and cooled as described in the above O₂-TPD experiment. Then the pretreated and cooled catalysts were kept at 30°C for a certain time with 1vol.% O₃/O₂. Then the resulting samples were further heated to 600°C under a He gas flow at a heating rate of 5°C min⁻¹.

Fouriertransforminfrared spectra (FT-IR) were recorded by Thermal Nicolet 6700 spectroscopy and the scanning range was 650-4000 cm^{-1} . The resolution was of 2 cm^{-1} . KBr was added to dilute the sample.

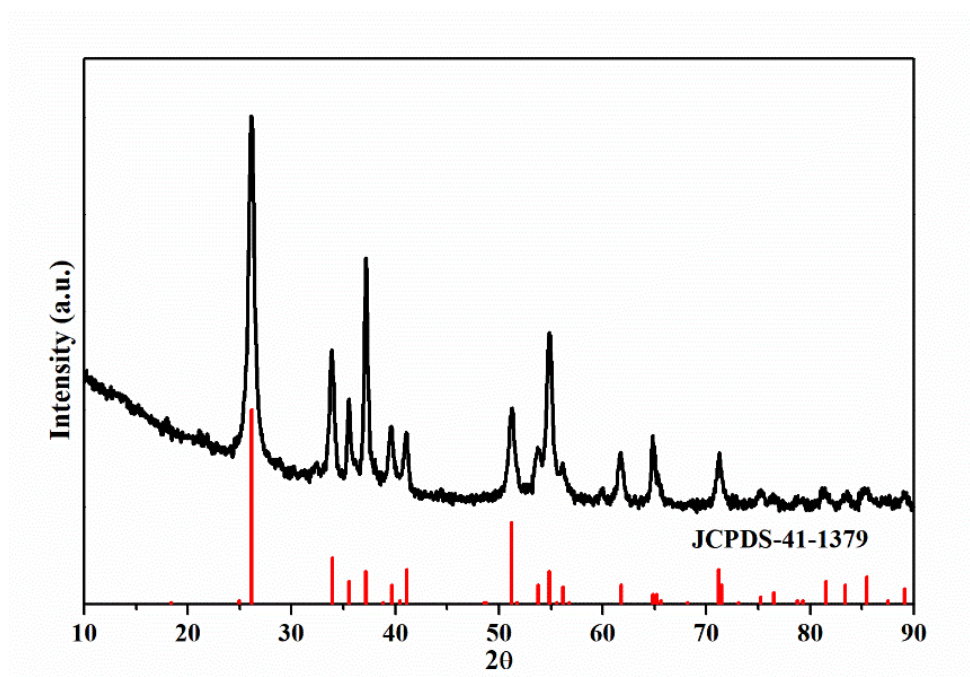


Figure S1. XRD patterns of the as-prepared γ -MnOOH

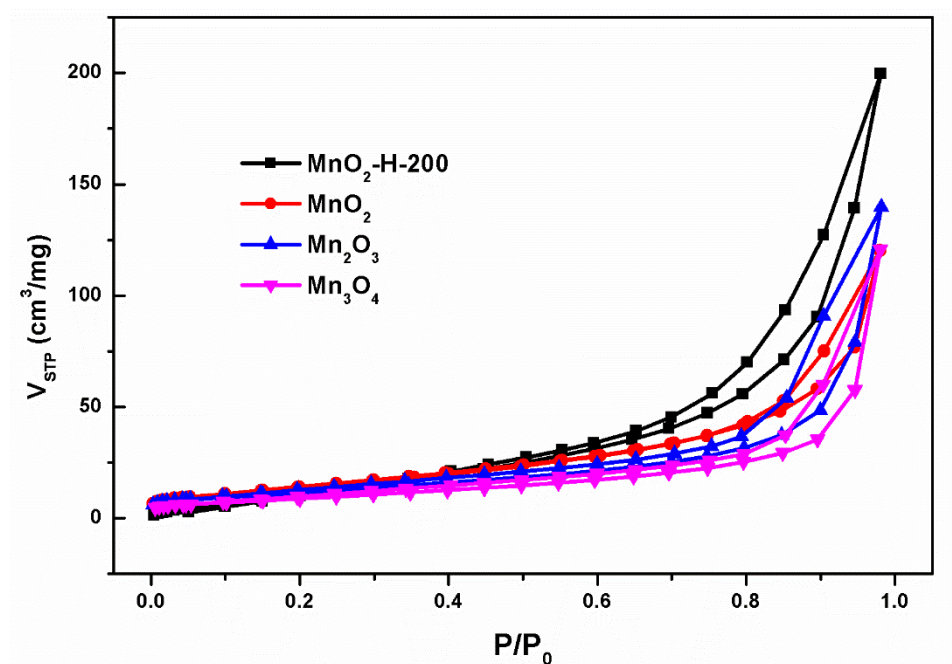


Figure S2. N₂ adsorption and desorption isotherms of the different MnO_x catalysts (MnO₂-H-200, MnO₂, Mn₂O₃ and Mn₃O₄)

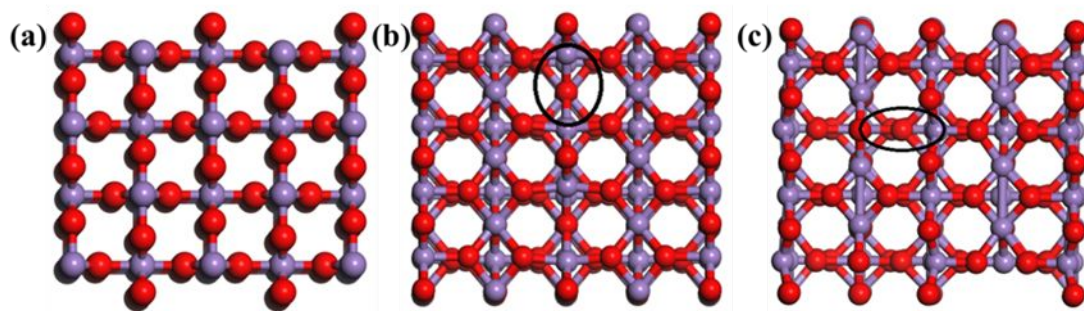


Figure S3. (a) the top plane view of β -MnO₂ (110), (b) and (c) the sites of oxygen vacancy

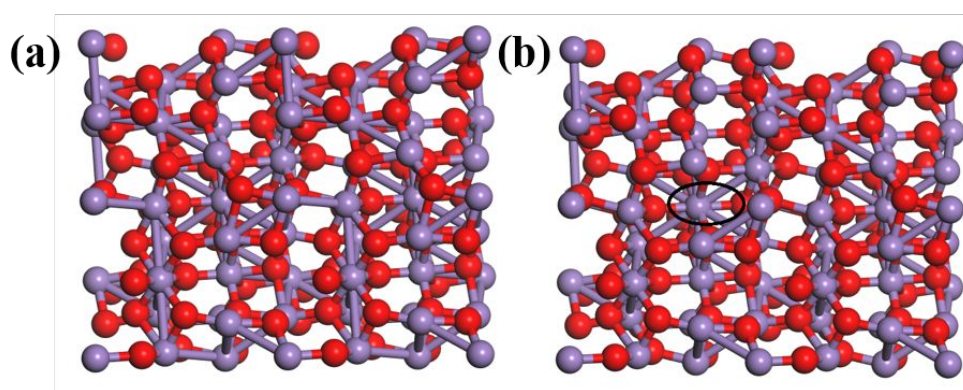


Figure S4. (a) the top plane view of Mn₂O₃ (211), (b) the sites of oxygen vacancy

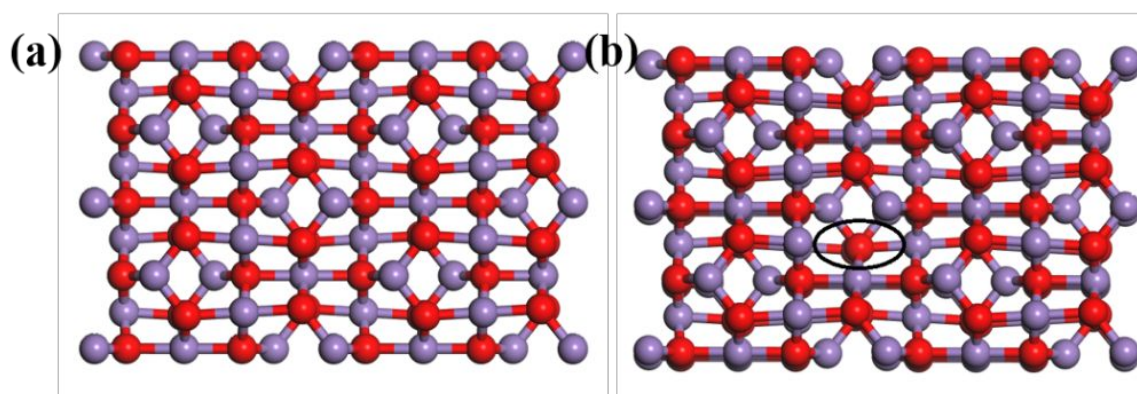


Figure S5. (a) the top plane view of Mn₃O₄ (200), (b) the sites of oxygen vacancy

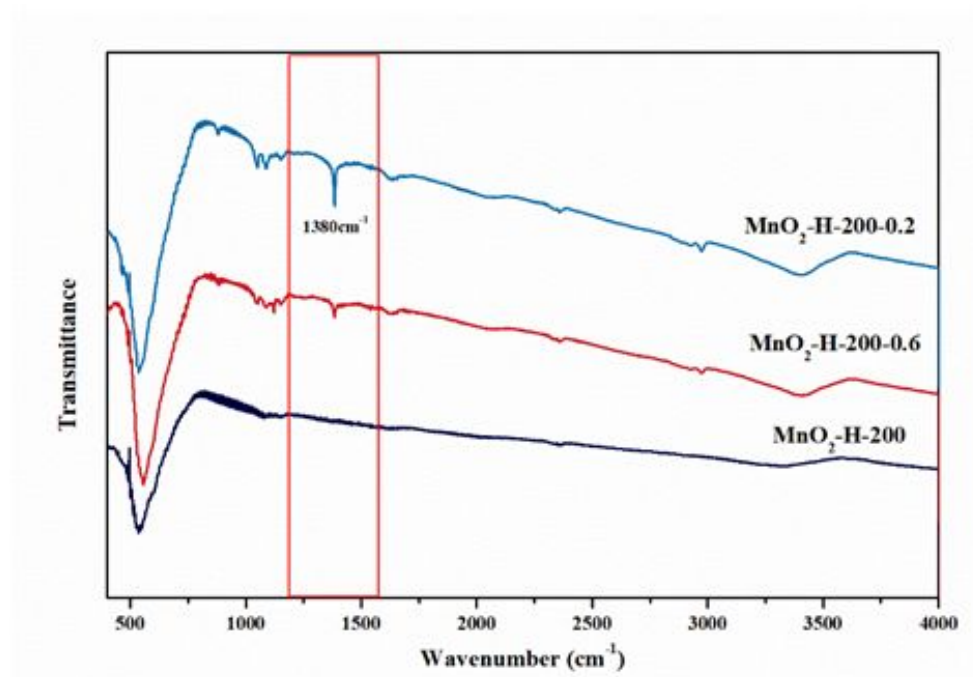


Figure S6. FT-IR spectra of MnO₂-H-200, MnO₂-H-200-0.6 and MnO₂-H-200-0.2.

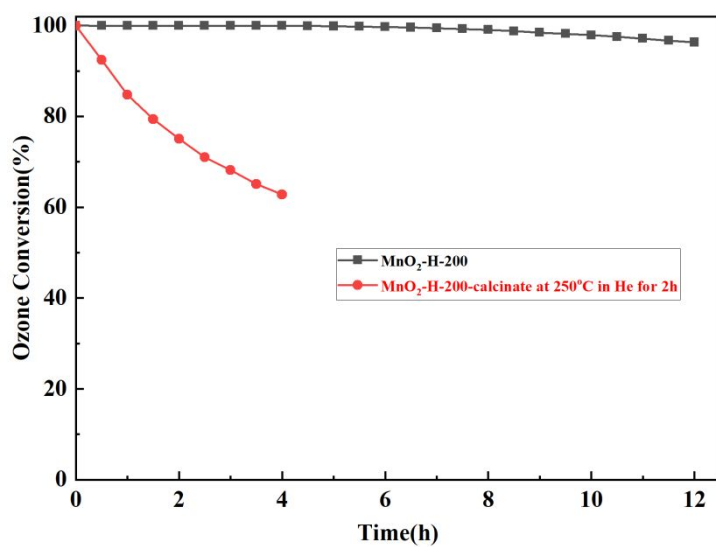


Figure S7. Ozone conversion over MnO₂-H-200 and the regenerated MnO₂-H-200

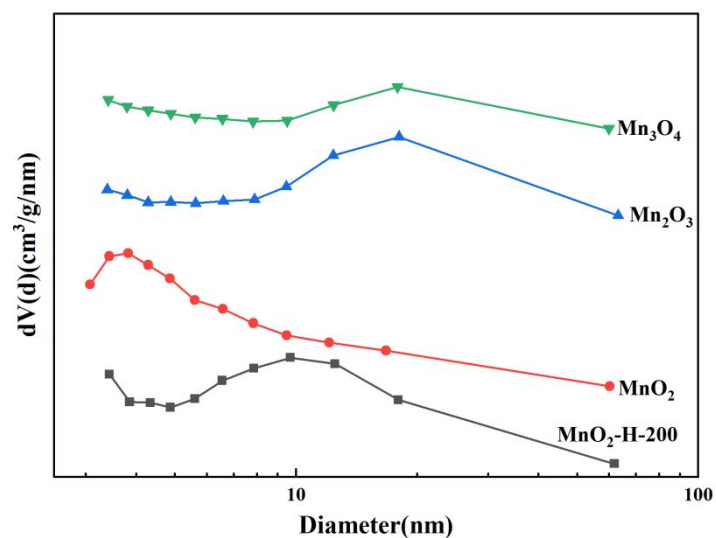


Figure S8. The pore size distribution for different MnO_x catalysts ($\text{MnO}_2\text{-H-200}$, MnO_2 , Mn_2O_3 and Mn_3O_4) calculated by BJH method

Table S1 Surface Area and pore size distribution of MnO_2 , Mn_2O_3 and Mn_3O_4

	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
MnO_2	54.4	0.180	3.4
Mn_2O_3	43.8	0.214	18.0
Mn_3O_4	34.8	0.183	18.9